

Ultrafast laser-induced birefringence in various porosity silica glasses: from fused silica to aerogel

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Abstract: We compare a femtosecond laser induced modification in silica matrices with three different degrees of porosity. In single pulse regime, the decrease of substrate density from fused silica to high-silica porous glass and to silica aerogel glass results in tenfold increase of laser affected region with the formation of a symmetric cavity surrounded by the compressed silica shell with pearl like structures. In multi-pulse regime, if the cavity produced by the first pulse is relatively large, the subsequent pulses do not cause further modifications. If not, the transition from void to the anisotropic structure with the optical axis oriented parallel to the incident polarization is observed. The maximum retardance value achieved in porous glass is twofold higher than in fused silica, and tenfold greater than in aerogel. The polarization sensitive structuring in porous glass by two pulses of ultrafast laser irradiation is demonstrated, as well as no observable stress is generated at any conditions.

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References and links

1. R. R. Gattass and E. Mazur, "Femtosecond laser micromachining in transparent materials," *Nat. Photonics* **2**(4), 219–225 (2008).
2. M. Beresna, M. Gecevičius, and P. G. Kazansky, "Polarization sensitive elements fabricated by femtosecond laser nanostructuring of glass," *Opt. Mater. Express* **1**(4), 783–795 (2011).
3. K. M. Davis, K. Miura, N. Sugimoto, and K. Hirao, "Writing waveguides in glass with a femtosecond laser," *Opt. Lett.* **21**(21), 1729–1731 (1996).
4. A. Marcinkevičius, S. Juodkazis, M. Watanabe, M. Miwa, S. Matsuo, H. Misawa, and J. Nishii, "Femtosecond laser-assisted three-dimensional microfabrication in silica," *Opt. Lett.* **26**(5), 277–279 (2001).
5. Y. Bellouard, A. Said, M. Dugan, and P. Bado, "Fabrication of high-aspect ratio, micro-fluidic channels and tunnels using femtosecond laser pulses and chemical etching," *Opt. Express* **12**(10), 2120–2129 (2004).
6. E. N. Glezer, M. Milosavljevic, L. Huang, R. J. Finlay, T.-H. Her, J. P. Callan, and E. Mazur, "Three-dimensional optical storage inside transparent materials," *Opt. Lett.* **21**(24), 2023–2025 (1996).
7. Y. Shimotsuma, M. Sakakura, P. G. Kazansky, M. Beresna, J. Qiu, K. Miura, and K. Hirao, "Ultrafast manipulation of self-assembled form birefringence in glass," *Adv. Mater.* **22**(36), 4039–4043 (2010).
8. J. Zhang, M. Gecevičius, M. Beresna, and P. G. Kazansky, "Seemingly unlimited lifetime data storage in nanostructured glass," *Phys. Rev. Lett.* **112**(3), 033901 (2014).
9. J. Zhang, A. Čerkauskaitė, R. Drevinskas, A. Patel, M. Beresna, and P. G. Kazansky, "Eternal 5D data storage by ultrafast laser writing in glass," in *Laser-Based Micro- and Nanoprocessing X*, U. Klotzbach, K. Washio, and C. B. Arnold, eds. (2016), p. 97360U.
10. M. Beresna, M. Gecevičius, and P. G. Kazansky, "Ultrafast laser direct writing and nanostructuring in transparent materials," *Adv. Opt. Photonics* **6**(3), 293 (2014).
11. R. Drevinskas, M. Beresna, J. Zhang, A. G. Kazanskii, and P. G. Kazansky, "Ultrafast laser-induced metasurfaces for geometric phase manipulation," *Adv. Opt. Mater.* **5**(1), 1600575 (2017).
12. S. K. Sundaram and E. Mazur, "Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses," *Nat. Mater.* **1**(4), 217–224 (2002).
13. P. Kazansky, H. Inouye, T. Mitsuyu, K. Miura, J. Qiu, K. Hirao, and F. Starrost, "Anomalous anisotropic light scattering in Ge-doped silica glass," *Phys. Rev. Lett.* **82**(10), 2199–2202 (1999).
14. Y. Shimotsuma, P. G. Kazansky, J. Qiu, and K. Hirao, "Self-organized nanogratings in glass irradiated by ultrashort light pulses," *Phys. Rev. Lett.* **91**(24), 247405 (2003).

15. E. Bricchi, B. G. Klappauf, and P. G. Kazansky, "Form birefringence and negative index change created by femtosecond direct writing in transparent materials," *Opt. Lett.* **29**(1), 119–121 (2004).
16. R. Taylor, C. Hnatovsky, and E. Simova, "Applications of femtosecond laser induced self-organized planar nanocracks inside fused silica glass," *Laser Photonics Rev.* **2**(1-2), 26–46 (2008).
17. J. Canning, M. Lancry, K. Cook, A. Weickman, F. Brisset, and B. Poumellec, "Anatomy of a femtosecond laser processed silica waveguide [Invited]," *Opt. Mater. Express* **1**(5), 998 (2011).
18. M. Lancry, B. Poumellec, J. Canning, K. Cook, J. C. Poulin, and F. Brisset, "Ultrafast nanoporous silica formation driven by femtosecond laser irradiation," *Laser Photonics Rev.* **7**(6), 953–962 (2013).
19. S. Richter, C. Miese, S. Döring, F. Zimmermann, M. J. Withford, A. Tünnermann, and S. Nolte, "Laser induced nanogratings beyond fused silica - periodic nanostructures in borosilicate glasses and ULETM," *Opt. Mater. Express* **3**(8), 1161 (2013).
20. M. Lancry, J. Canning, K. Cook, M. Heili, D. R. Neuville, and B. Poumellec, "Nanoscale femtosecond laser milling and control of nanoporosity in the normal and anomalous regimes of GeO₂-SiO₂ glasses," *Opt. Mater. Express* **6**(2), 321 (2016).
21. S. S. Fedotov, R. Drevinskas, S. V. Lotarev, A. S. Lipatiev, M. Beresna, A. Čerkauskaitė, V. N. Sigaev, and P. G. Kazansky, "Direct writing of birefringent elements by ultrafast laser nanostructuring in multicomponent glass," *Appl. Phys. Lett.* **108**(7), 071905 (2016).
22. V. R. Bhardwaj, E. Simova, P. P. Rajeev, C. Hnatovsky, R. S. Taylor, D. M. Rayner, and P. B. Corkum, "Optically produced arrays of planar nanostructures inside fused silica," *Phys. Rev. Lett.* **96**(5), 057404 (2006).
23. M. Beresna, M. Gecevičius, P. G. Kazansky, T. Taylor, and A. V. Kavokin, "Exciton mediated self-organization in glass driven by ultrashort light pulses," *Appl. Phys. Lett.* **101**(5), 53120 (2012).
24. F. Liang, R. Vallée, and S. Chin, "Physical evolution of nanograting inscription on the surface of fused silica," *Opt. Mater. Express* **2**(7), 1244–1250 (2012).
25. Y. Liao, J. Ni, L. Qiao, M. Huang, Y. Bellouard, K. Sugioka, and Y. Cheng, "High-fidelity visualization of formation of volume nanogratings in porous glass by femtosecond laser irradiation," *Optica* **2**(4), 329 (2015).
26. F. Zimmermann, A. Plech, S. Richter, A. Tünnermann, and S. Nolte, "The onset of ultrashort pulse-induced nanogratings," *Laser Photonics Rev.* **8**, 1–8 (2016).
27. A. Rudenko, J.-P. Colombier, and T. E. Itina, "From random inhomogeneities to periodic nanostructures induced in bulk silica by ultrashort laser," *Phys. Rev. B* **93**(7), 75427 (2016).
28. Y. Liao, Y. Shen, L. Qiao, D. Chen, Y. Cheng, K. Sugioka, and K. Midorikawa, "Femtosecond laser nanostructuring in porous glass with sub-50 nm feature sizes," *Opt. Lett.* **38**(2), 187–189 (2013).
29. Y. Liao, W. Pan, Y. Cui, L. Qiao, Y. Bellouard, K. Sugioka, and Y. Cheng, "Formation of in-volume nanogratings with sub-100-nm periods in glass by femtosecond laser irradiation," *Opt. Lett.* **40**(15), 3623–3626 (2015).
30. A. Soleimani Dorcheh and M. H. Abbasi, "Silica aerogel; synthesis, properties and characterization," *J. Mater. Process. Technol.* **199**(1-3), 10–26 (2008).
31. J. Sun, J. P. Longtin, and P. M. Norris, "Ultrafast laser micromachining of silica aerogels," *J. Non-Cryst. Solids* **281**(1-3), 39–47 (2001).
32. B. Yalçay, Y. Morova, K. Dincer, Y. Ozbakir, A. Jonas, C. Erkey, A. Kiraz, and S. Akturk, "Versatile liquid-core optofluidic waveguides fabricated in hydrophobic silica aerogels by femtosecond-laser ablation," *Opt. Mater. (Amst.)* (2015).
33. E. N. Glezer and E. Mazur, "Ultrafast-laser driven micro-explosions in transparent materials," *Appl. Phys. Lett.* **71**(7), 882–884 (1997).
34. S. Juodkazis, H. Misawa, T. Hashimoto, E. G. Gamaly, and B. Luther-Davies, "Laser-induced microexplosion confined in a bulk of silica: Formation of nanovoids," *Appl. Phys. Lett.* **88**(20), 38–41 (2006).
35. S. Juodkazis, K. Nishimura, S. Tanaka, H. Misawa, E. G. Gamaly, B. Luther-Davies, L. Hallo, P. Nicolai, and V. Tikhonchuk, "Laser-induced microexplosion confined in the bulk of a sapphire crystal: evidence of multimegabar pressures," *Phys. Rev. Lett.* **96**(16), 166101 (2006).
36. L. Rapp, B. Haberl, J. E. Bradby, E. G. Gamaly, J. S. Williams, and A. V. Rode, "Fundamentals of laser-assisted micro- and nanotechnologies," **195**, 3–27 (2014).
37. A. Mermillod-Blondin, J. Bonse, A. Rosenfeld, I. V. Hertel, Y. P. Meshcheryakov, N. M. Bulgakova, E. Audouard, and R. Stoian, "Dynamics of femtosecond laser induced voidlike structures in fused silica," *Appl. Phys. Lett.* **94**(4), 41911 (2009).
38. R. Stoian, K. Mishchik, G. Cheng, C. Mauclair, C. D'Amico, J. P. Colombier, and M. Zamfirescu, "Investigation and control of ultrafast laser-induced isotropic and anisotropic nanoscale-modulated index patterns in bulk fused silica," *Opt. Mater. Express* **3**(10), 1755 (2013).
39. G. Poelz and R. Riethmüller, "Preparation of silica aerogel for Cherenkov counters," *Nucl. Instrum. Methods Phys. Res.* **195**(3), 491–503 (1982).
40. I. Hachisu, T. Matsuda, K. Nomoto, and T. Shigeyama, "Mixing in ejecta of supernovae. II. Mixing width of 2D Rayleigh-Taylor instabilities in the helium star models for type Ib/Ic supernovae," *Astron. Astrophys. Suppl. Ser.* **104**, 341–364 (1994).
41. W. H. Cabot and A. W. Cook, "Reynolds number effects on Rayleigh-Taylor instability with possible implications for type Ia supernovae," *Nat. Phys.* **2**(8), 562–568 (2006).
42. A. Vogel, N. Linz, S. Freidank, and G. Paltauf, "Femtosecond-laser-induced nanocavitation in water: implications for optical breakdown threshold and cell surgery," *Phys. Rev. Lett.* **100**(3), 038102 (2008).

43. E. G. Gamaly, S. Juodkazis, K. Nishimura, H. Misawa, B. Luther-Davies, L. Hallo, P. Nicolai, and V. T. Tikhonchuk, "Laser-matter interaction in the bulk of a transparent solid: Confined microexplosion and void formation," *Phys. Rev. B – Condens. Matter Mater. Phys.* **73**(21), 1–15 (2006).
44. L. Sudrie, A. Couairon, M. Franco, B. Lamouroux, B. Prade, S. Tzortzakakis, and A. Mysyrowicz, "Femtosecond laser-induced damage and filamentary propagation in fused silica," *Phys. Rev. Lett.* **89**(18), 186601 (2002).
45. Y. Dai, A. Patel, J. Song, M. Beresna, and P. G. Kazansky, "Void-nanograting transition by ultrashort laser pulse irradiation in silica glass," *Opt. Express* **24**(17), 19344–19353 (2016).
46. O. Dematteo Caulier, K. Mishchik, B. Chimier, S. Skupin, A. Bourgeade, C. Javaux Léger, R. Kling, C. Hönniger, J. Lopez, V. Tikhonchuk, and G. Duchateau, "Femtosecond laser pulse train interaction with dielectric materials," *Appl. Phys. Lett.* **107**(18), 181110 (2015).
47. N. M. Bulgakova, V. P. Zhukov, S. V. Sonina, and Y. P. Meshcheryakov, "Modification of transparent materials with ultrashort laser pulses: What is energetically and mechanically meaningful?" *J. Appl. Phys.* **118**(23), 233108 (2015).
48. C. Corbari, A. Champion, M. Gecevičius, M. Beresna, Y. Bellouard, and P. G. Kazansky, "Femtosecond versus picosecond laser machining of nano-gratings and micro-channels in silica glass," *Opt. Express* **21**(4), 3946–3958 (2013).

1. Introduction

Modification of transparent materials with ultrafast laser pulses has attracted interest due to its relevance to a wide range of applications including polarization sensitive flat optics, waveguides, microfluidic devices, optical data storage [1–11]. The key advantage of using femtosecond pulses for direct laser writing, as opposed to longer pulses, is that they can rapidly deposit energy in solids with high precision. The light is absorbed, and the optical excitation ends before the surrounding lattice is perturbed, which results in highly localized modification without collateral material damage [1,12].

Under certain conditions, the interaction of femtosecond pulses with silica is known to induce self-assembled nanostructures with a lamellae-like oxygen deficient regions oriented perpendicular to the incident beam polarization [13,14]. In 2004 Bricchi et al. demonstrated that such nanostructures, due to the sub-wavelength periodicity, behave as a uniaxial birefringent material where the optical axis is parallel to the orientation of laser polarization, and exhibit birefringence comparable to quartz crystals [15]. It was suggested that these nanostructures are composed of parallel planar nano-cracks [16], or nanoporous planes filled with decomposed SiO_2 and oxygen [17,18]. More recently it was demonstrated that such anisotropic nanostructures can be realized in various multicomponent glasses [19–21].

Despite many hypotheses to explain the mechanism of the peculiar self-organization, the formation of the periodic nanostructures remains under debate giving the ideas of seeding processes governed by the randomly distributed inhomogeneity [14,16,22–27]. Therefore, intuitively it could be expected that the higher degree of porosity of the substrate could promote the growth of the periodic structure by lowering the number of pulses. Recently, the single isolated nanoplane was demonstrated in porous glass fabricated from the phase-separated alkali-borosilicate glass and combining the experimental results with the concept of the surface plasma wave excitation, the significance of the seed structures was suggested [25,28,29].

It is interesting to exploit the possibility of nanograting formation in highly porous silica materials such as silica aerogel [30]. More than a decade ago, it was demonstrated that due to the ultra-low thermal conductivity aerogel can be precisely ablated by the femtosecond pulses [31]. However, despite recent demonstrations of aerogel-based optofluidic waveguides [32], systematic studies of ultrafast laser induced modifications in aerogel and in particular a nanograting induced birefringence have not been reported.

In this paper, we compare femtosecond laser-induced modifications in silica glasses with different densities including fused silica, porous glass, and aerogel. In single-pulse regime, the symmetric cavity surrounded by the compressed silica glass is formed, while in the multi-pulse regime, the transition from void to the anisotropic structure with the optical axis oriented parallel to the incident polarization is observed in all glasses. We identify that such transition depends on the density of silica substrate, and could be produced by 2-3 pulses in

porous glass with pores smaller than 5 nm. The maximum retardance value achieved in porous glass is twofold and tenfold higher than in fused silica and silica aerogel, respectively.

2. Materials and methods

Experiments were carried out with (1) commercially available synthetic fused silica (Shin-Etsu, Viosil) with mass density of $\rho_0 = 2.2 \text{ g/cm}^3$, Young modulus $Y = 74.5 \text{ GPa}$, and 1.45 index of refraction; (2) high-silica (96%) porous glass (Corning, Vycor) with mass density of $\rho_0 = 1.5 \text{ g/cm}^3$, Young modulus $Y = 17.5 \text{ GPa}$, 1.33 index of refraction, and pores size less than 5 nm; (3) silica aerogel glass with mass density of $\rho_0 = 0.25 \text{ g/cm}^3$, Young modulus $Y = 10 \text{ MPa}$, and 1.05 index of refraction; (4) sol-gel derived porous silica glass (Geltech, Gelsil) with pores size of 2.5 nm, 7.5 nm and 20 nm. Optical transmission higher than 95% is measured for all pristine glasses at the wavelength of 1030 nm.

Samples were irradiated with a ytterbium-doped potassium gadolinium tungstate (Yb:KGW) based mode-locked regenerative amplified femtosecond laser system PHAROS (Light Conversion Ltd.) operating at a wavelength of 1030 nm (photon energy $\sim 1.2 \text{ eV}$) with the repetition rate of 200 kHz.

In the case of single dot modification, from single pulse to trains up to 100 pulses with the pulse duration of 320 fs and energy varying from 0.02 μJ to 0.8 μJ were focused via a 0.55 NA objective lens 100 μm below the surface of a silica sample, which was mounted onto an XYZ linear air-bearing translation stage (Aerotech Ltd.). The estimated spot radius of the laser beam in focus was $\omega_0 \approx 0.6 \mu\text{m}$.

In the case of scanned (line) modification, maintaining the same focusing conditions and pulse density of ~ 100 pulses per spot size, 50 μm long lines were imprinted at a constant translation speed of 2 mm/s. The dependences of induced retardance on pulse energy varying from 0.02 μJ to 0.8 μJ and pulse duration from 320 fs to 4 ps were mapped.

The laser induced birefringence, i.e. retardance and its slow axis, was characterized and visualized with the quantitative birefringence measurement system (CRi Abrio; Olympus BX51) operating at 546 nm. Irradiated regions were also analysed using digital holographic microscope (Lyncée tec) that additionally provides quantitative phase measurements, which allows to estimate the induced index change. The imaging of laser-induced structures was performed with a scanning electron microscope (SEM) Zeiss Evo50 and optical transmission microscope Olympus BX51.

3. Results and discussion

3.1 Single-pulse imprinting of dots

The formation of laser-induced periodic nanostructures and related birefringence is an accumulative process requiring a multi-pulse irradiation. In the single pulse regime, the diameter of the dots induced by 320 fs pulses with the energy of 0.2 μJ in silica aerogel is roughly six times larger than the spot diameter of the focused laser beam [Fig. 1(a)]. The energy is absorbed in a small volume producing a pressure which subsequently drives a shock wave and stress exceeding the Young modulus of the material. The strong spherical shock wave starts to propagate outside the centre of symmetry of the absorbed energy region compressing the material [33–38]. At the same time, a rarefaction wave propagates to the centre of symmetry decreasing the density in the area of the energy deposition. The shock wave stops when the pressure behind the shock front becomes comparable with the Young modulus. The diameters of the void D_v and shock affected D_a regions were depicted from the cross section plane normal to the direction of light propagation.

Considering the measurement of optical path difference [Fig. 1(a) right] and the relevant axial cross section of the structure induced in silica aerogel, the refractive index of the densified area and the central part of the void exhibit values of ~ 1.07 and ~ 1.03 , respectively, which is in a good agreement with the calculation of refractive index based on material

density [39]. In addition, the granular pearl-like structure of the shell, similar to that observed in water splash, confinement fusion or supernova explosion, is believed to be the result of Rayleigh instability [40–42].

Here, the process of the rarefaction and densification is based on the mass and energy conservation. The distance at which the front of the shock wave effectively stops can be determined by assuming that the internal energy of the material with volume of $4/3\pi r^3$ is nearly equivalent to the absorbed laser pulse energy: $4/3\pi Y r_{stop}^3 \approx E_{abs}$. Then the laser affected region $D_a \approx 2r_{stop}$ ($D_a \approx c \times D_v$) with the void diameter D_v are fitted to experimental values [Fig. 1(b)] using the above arguments by the following formula [34,43]:

$$D_v = \frac{1}{c} \sqrt[3]{\frac{6aE_p}{\pi Y b}}, \quad (1)$$

where a represents the fraction of the pulse energy E_p absorbed by the material; Y is Young modulus; b shows the ratio of diameter and length of the affected region.

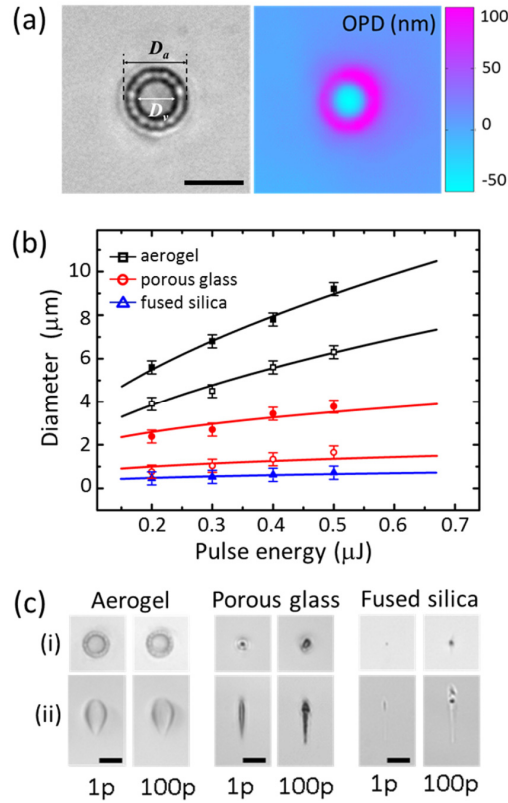


Fig. 1. Laser-induced modification in silica glasses. (a) Optical transmission (left) and optical path difference (right) top view images defining the laser affected region D_a and the lateral void region D_v in silica aerogel induced by a single pulse irradiation. (b) The diameter of D_a (closed symbols) and D_v (open symbols) as a function of laser pulse energy. Black, red and blue colours represent the modification in aerogel, porous glass and fused silica, respectively. Fitting dependences (solid lines) were calculated using Eq. (1). (c) Optical transmission (i) top view and (ii) side viewed images of single dot modification in silica aerogel, porous glass and fused silica, induced by 1 pulse and 100 pulses irradiation. The laser beam in (c,ii) was propagating from top to bottom. The pulse energy in (a) and (c) was set to 0.2 μJ. Scale bars are 5 μm.

If the Young modulus remains constant over the processing time, the corresponding energy density indicates that the material has to be fully ionized in order to induce modification [34–36,43]. However, theoretical and experimental studies on femtosecond laser pulses induced damage and propagation in fused silica dispute this assumption as void formation could happen in the regions where electron density is below critical [44,45]. In this scenario, the strength (Young modulus) of the solid has to decrease due to the softening of the heated material, where the ordinary cavitation or compaction based on thermomechanical processes could take place. The value of local temperatures after the single pulse irradiation is still questionable [46,47], and therefore the dynamics of the void formation is out of the scope in this work.

Young modulus for silica aerogel is almost four orders of magnitude lower than for fused silica. Thus, if ~100% of the pulse energy is absorbed, it follows from Eq. (1) that the void diameter will be 20 times larger in silica aerogel than in fused silica. However, the experimental ratio of 8:1 [Fig. 1(b)] clearly indicates that the absorbed energy is significantly lower. The transmission was measured 30% in fused silica, 25% in porous glass and 55% in silica aerogel at pulse energy of 0.5 μJ . Assuming that the Young modulus does not change over the processing time, we estimate that only ~10%, ~20% and ~0.5% of the pulse energy is absorbed to produce the corresponding void structure in fused silica, porous glass and silica aerogel, respectively. However, if the Young modulus decreases over the processing time, the fitting dependences of void diameter [Eq. (1)] will be valid only proportionally reducing the absorbed energy.

Interesting to note that in porous glass the part of the energy absorbed and consumed to produce modification is twice higher than in fused silica. The modification in fused silica appears before the focus [Fig. 1(c)]. A fraction of the energy is absorbed to induce the cavitation, while the majority of the energy is absorbed and scattered in the large volume. On the other hand, in lower density silica glasses the void geometry follows the intensity profile. This indicates that most of the energy in aerogel and porous glass is delivered close to the focus, and due to the lower volume, density and Young modulus the smaller fraction of the pulse energy is used for cavitation.

After the modification, glass initially confined in a volume with diameter D_a resides in an ellipsoidal layer in between D_a and D_v , which has a density of $\rho = \rho_0 \delta$ with $\delta > 1$ [34]. Thus, the ratio of D_a and D_v can be expressed as:

$$c = \sqrt[3]{\frac{\delta}{\delta-1}}. \quad (2)$$

Applying the experimental values of $c^{\text{aerogel}} \approx 1.4$ and $c^{\text{porous}} \approx 1.8$, the densified material shows ~1.6 and ~1.2 times higher density than the pristine silica aerogel and porous glass, respectively. Whereas, the typical compression ratio of 1.14 is reported for fused silica [34].

3.2 Multi-pulse imprinting of dots

In the multi-pulse regime, the subsequent irradiation of aerogel does not affect the radius of the modification induced by the first pulse, confirming that the initial pulse induces a void larger than the irradiated volume. The size of the laser affected region remains the same with the diameter of ~5.5 μm and length of ~10 μm continuously delivering up to 100 pulses with the pulse energy of 0.2 μJ [Fig. 1(c)]. However, in the case of porous glass and fused silica, the size of the modification increases with the number of pulses. The change of diameter from 2.2 μm to 3 μm and length from 8.5 μm to 10 μm in porous glass, and diameter from 0.5 μm to 1 μm and length from 8.5 μm to 12.5 μm in fused silica were observed [Fig. 1(c)].

Based on the quantitative birefringence measurements, the retardance of a single dot modification in all glasses was mapped as a function of pulse energy and number of pulses [Figs. 2 and 3]. The resulting retardance maps can be divided into several regions with

different types of modification. In fused silica [Fig. 2(a)], when energy varies from 0.04 μJ to 0.1 μJ , the uniform anisotropic structure such as nanogratings oriented perpendicular to the incident laser beam polarization are formed (region (i)). Such structures with retardance of up to 5 nm are observed after the irradiation with 5 pulses. However, the consistent slow axis orientation requires 8-12 pulses.

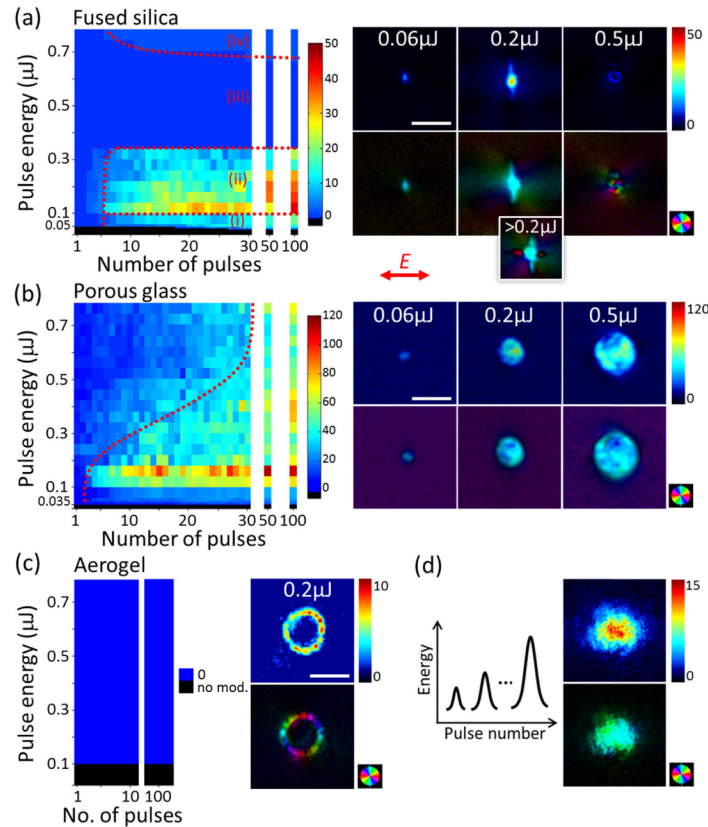


Fig. 2. Femtosecond laser-induced modification in different density silica glasses: (a) fused silica, (b) porous glass (Vycor), and (c,d) silica aerogel. Colour maps on the left in (a-c) show the resulting retardance of polarization sensitive structures as a function of pulse energy and number of pulses. Colour bars are linear retardance scales in nanometres; the value of zero corresponds to the voids, i.e. polarization independent structures; black color indicates the condition below the modification threshold. Edge and stress-induced birefringence are not considered. In (a), red dotted line marks the regions with a different type of modification: (i) – nanogratings, (ii) – nanogratings with polarization sensitive cracks, (iii) – voids, (iv) – voids with randomly oriented cracks. In (b), the red dotted line indicates the boundary between the laser-induced void accompanied by the anisotropic structure and its transition to the uniform anisotropic material, i.e. nanogratings. On the right in (a-c), top view images of the corresponding retardance (top) and its slow axis (bottom) of structures induced by 100 pulses at a certain constant pulse energy. (d) Aerogel sample irradiated by 100 pulses with pulse energy increasing from 0.02 μJ to 0.38 μJ . Red arrow defines the polarization state of the incident laser beam. Colour bars are linear retardance scales in nanometres. Pseudo colours (bottom insets) indicate the orientation of the slow axis. Scale bar is 5 μm .

At energy greater than 0.1 μJ , the nanograting is accompanied by a crack oriented perpendicular to the incident laser beam polarization, and at energy greater than 0.2 μJ , two cracks are formed in the direction parallel and perpendicular to the incident laser beam polarization (region (ii)). In this regime, the highest values of retardance are achieved reaching up to 50 nm with irradiation of 100 pulses. When the pulse energy exceeds the value

of 0.3 μJ , the cavity induced by the first pulse is too large to be re-organized into the polarization sensitive structure by the subsequent pulses. Specifically, the material is pushed away from the focal region. Thus, at energies higher than 0.3 μJ , symmetric voids (region (iii)), and at energies higher than 0.7 μJ , voids with randomly oriented cracks (region (iv)) are formed. Same symmetric cavities are induced at all energies higher than the modification threshold if irradiating with less than 5 pulses. Such structure holds only edge and/or stress-induced birefringence, which is subtracted from the retardance maps.

In porous glass [Figs. 2(b) and 3(a)], the smooth transition from void structure to uniform birefringent material with the optical axis (slow axis) oriented parallel (perpendicular) to the incident laser beam polarization is observed. Close to the modification threshold ($>0.035 \mu\text{J}$), this transition takes around 2-3 pulses [Fig. 3(b)], while at energies higher than 0.5 μJ the transition from void to uniform anisotropic material requires tens of pulses. In fact, the less dense porous glass, the more pulses have to be delivered. Moreover, if the pores size is increased, e.g. to $\sim 20 \text{ nm}$, the parameter window of the induced birefringent structure shrinks significantly [Fig. 3(a)]. This clearly indicates that the modification process is strongly dependent on the void diameter induced by the first pulse, as the diameter is changing with the glass density. When the size of pores increases from 2.5 nm to 7.5 nm and 20 nm, the consistent anisotropic structure with the maximum retardance tends to form at lower energies, around 0.11 μJ , 0.07 μJ and 0.06 μJ for each porosity respectively. Operating close to the threshold energy, the size of modification in porous glass becomes comparable to the one in fused silica, though the value of retardance in porous glass is twice higher reaching the value up to 120 nm for pores size less than 5 nm [Figs. 2(b) and 3(a)]. This value drops to 30 nm as the porosity is increased [Fig. 3(a)]. No stress generated at any conditions was observed, what could be beneficial for potential applications in three-dimensional printing.

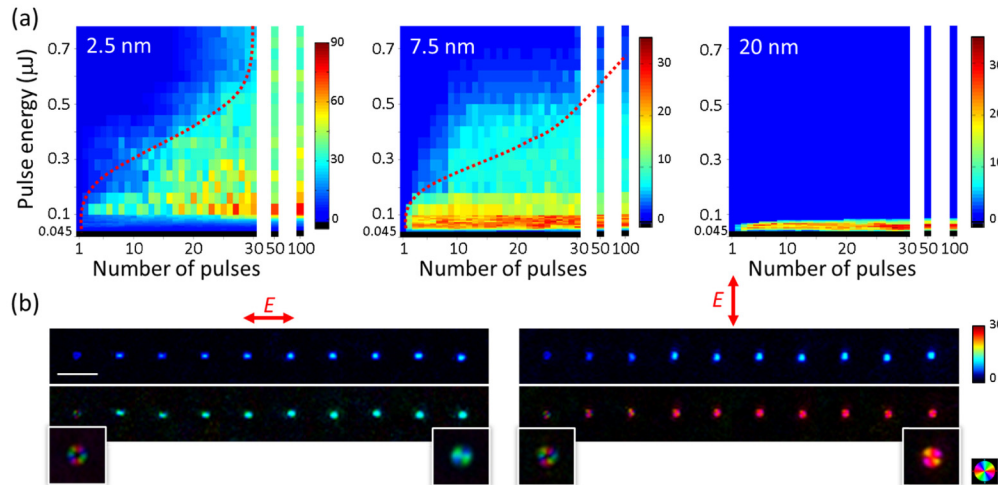


Fig. 3. (a) Retardance maps of polarization sensitive structures induced in sol-gel derived porous glass with pores size of 2.5 nm, 7.5 nm, and 20 nm. Red dotted lines show the approximate boundary between the laser-induced void accompanied by the anisotropic structure and its transition to the uniform anisotropic material, i.e. nanogratings. Colour bars are linear retardance scales in nanometres; the value of zero corresponds to the void, i.e. polarization independent, structure; black colour indicates the condition below the modification threshold. Stress and edge induced birefringence are not considered. (b) Evolution of the optical anisotropy in silica sample with the pores size of 2.5 nm, for two orthogonal polarizations. Images indicate retardation (top) and its slow axis (bottom) induced by 1 to 10 pulses when the pulse energy was fixed at 0.06 μJ . Insets represent the slow axis of 3x magnified structures induced by 1 and 10 pulses. Red arrows define the polarization state of the incident laser beam. Colour bars are linear retardance scales in nanometres. Pseudo colours (bottom insets) indicate the orientation of the slow axis. Scale bar is 5 μm .

In silica aerogel no modification is observed below the energy of 0.1 μJ ; above this threshold, the void structure is formed [Fig. 2(c)]. The shell of the compressed silica exhibits low birefringence with the azimuthally variant slow axis, what corresponds to the edge birefringence. Despite the diameter change, qualitatively the structure does not depend on the pulse energy and number of pulses. This clearly indicates that the subsequent pulses do not interact with the initially modified material. In this case, we have introduced direct densification experiment to avoid the cavitation effect in aerogel. We used a sequence of 100 laser pulses with linearly increasing pulse energy [Fig. 2(d)], keeping the total deposited energy the same as was used for 100 pulses with constant energy of 0.2 μJ [Fig. 2(c)]. Starting with the first low energy pulse (0.02 μJ), which is not sufficient to produce any observable modification, the pulse energy was increased up to 0.38 μJ . Thus, the material is gradually densified, and later the form birefringence is induced. The uniform anisotropic structure with retardance as high as 15 nm and slow axis oriented perpendicular to the incident laser beam polarization is produced.

3.3 Single and multi-scan laser writing

In the case of scanned (line) modification, top and side view images of silica aerogel demonstrate that the first pulse always produces a void similar to that observed in the case of single dot modification [Fig. 4]. Due to the sample translation, the subsequent incoming pulses always interact with the already modified region, thus causing the transition from void to polarization sensitive structure. In all glasses including silica aerogel, porous glass and fused silica the maximum induced retardance is 1.25-1.8 times higher compared to the dot modification with the same pulse density. This could be attributed to the seeding effect when every further pulse effectively continues the formation of pre-defined structure.

In silica aerogel the void is frozen at the beginning of the line, in porous glass the void is not clearly expressed as it is transformed into the anisotropic structure, and in fused silica it is transformed into the anisotropic structure and reproduced at the end of the scanned line imitating the dragging effect [Figs. 4(a) and 4(b)]. Despite an order of magnitude difference in the measured retardance value, the side view images of the scanned lines induced in porous and aerogel glasses are virtually same as the retardance is spread along the modification area [Figs. 4(c) and 4(d)]. In fused silica higher retardance value is localized at the top part of the line modification correlating with the results of the single dot modification.

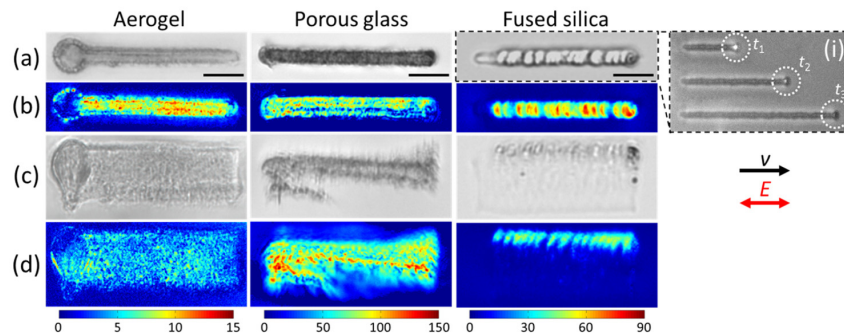


Fig. 4. (a,c) Optical transmission and (b,d) retardance, (a,b) top and (c,d) side view, images of laser written lines in silica aerogel, porous glass and fused silica. The laser beam in (c,d) was propagating from top to bottom. The pulse energy and pulse duration were fixed at 0.2 μJ and 320 fs. Inset (i) indicates the movement of the laser-induced cavity inside fused silica. Top view snapshots were taken at t_1 , t_2 , t_3 points in time during the writing process. Colour bars are linear retardance scales in nanometres. Black and red arrows indicate the writing direction and polarization state of the incident beam, respectively. Scale bar is 10 μm .

As the density in silica aerogel is lower compared to fused silica and porous glass, micrometre size voids are produced along the scanned line. One can see that when the

polarization is perpendicular to the writing direction [Fig. 5(a)], the single void of about $5\ \mu\text{m}$ length is formed with a sharp $2\ \mu\text{m}$ plane structure at the top and a dull $0.8\ \mu\text{m}$ plane at the bottom part of the structure. In case of polarization oriented parallel to the writing direction, the void with the length of $3\ \mu\text{m}$, and additional plane at the top with the length of $2.5\ \mu\text{m}$ are observed [Fig. 5(b)]. We also identify that the induced plane structures are oriented perpendicular to the incident polarization. The width of the voids is $\sim 0.8\ \mu\text{m}$, which is an order of magnitude wider than the observed in porous glass [28]. Same polarization sensitive structuring is observed when the scanned lines overlap [Fig. 5(c) and 5(d)]. The length of the modification is around $7\ \mu\text{m}$, including $2.5\ \mu\text{m}$ planes located at the top and bottom of the structure.

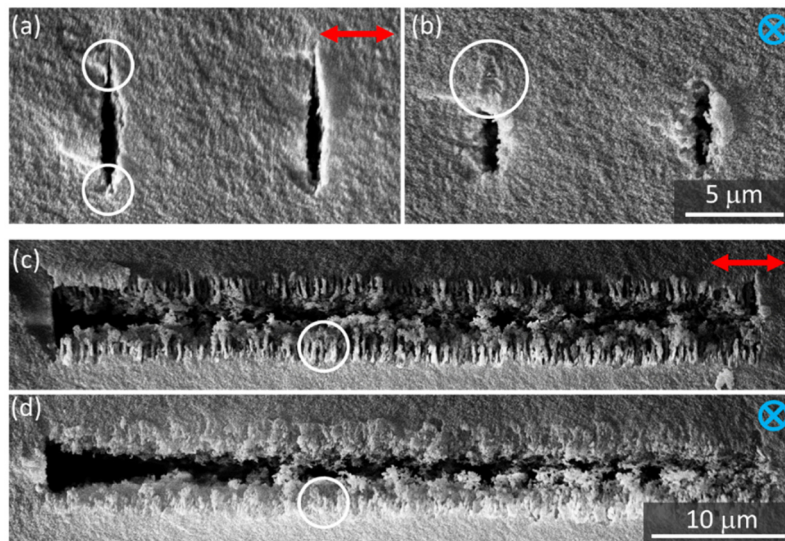


Fig. 5. SEM side views images of the lines written in silica aerogel. The interline distance was set to (a,b) $10\ \mu\text{m}$ and (c,d) $0.5\ \mu\text{m}$. The incident polarization was oriented perpendicular (red arrow in (a,c)) and parallel (blue cross in (b,d)) to the writing direction (normal to image plane). The laser beam was propagating from top to bottom. The pulse energy and pulse duration were fixed at $0.2\ \mu\text{J}$ and $320\ \text{fs}$. White open circles mark the regions with polarization sensitive structures. Scale bars: $5\ \mu\text{m}$ and $10\ \mu\text{m}$.

To compare the scanned lines in silica aerogel, porous glass and fused silica, the retardance maps as a function of pulse energy and pulse duration were plotted on a logarithmic scale [Fig. 6(a)]. Both porous glass and fused silica exhibit threshold energy of $0.04\ \mu\text{J}$ and $0.06\ \mu\text{J}$ at $320\ \text{fs}$, respectively, while silica aerogel shows the increased threshold energy of around $0.15\ \mu\text{J}$. The retardance maps for aerogel and porous glass can be identified as having high and low-value regions depending on the pulse duration. Retardance starts dropping at around $1\text{--}2\ \text{ps}$, showing the highest values of $30\ \text{nm}$ in silica aerogel and $140\ \text{nm}$ in porous glass at $320\ \text{fs}$. In the picosecond regime, the retardance drops significantly to less than 20% . This is most likely due to the heating taking place during the picosecond timescale that can lead to excessive stress and the collateral damage of the material [1,48]. Such processes could hinder the porosity of the glass, making it difficult to induce regular structures.

In fused silica, the induced retardance is almost constant over the full range of pulse durations with the maximum value of $80\ \text{nm}$ at around $2.5\ \text{ps}$ [Fig. 6(a)]. However, in the picosecond regime, the uniformity of the structure in fused silica as well as in lower density glasses drops. The VIS-NIR transmission of $80\text{--}90\%$ at $320\ \text{fs}$ decreases to less than $40\text{--}60\%$ at $1\ \text{ps}$. In this case, the retardance value is compensated by stronger modification typical for picosecond pulses.

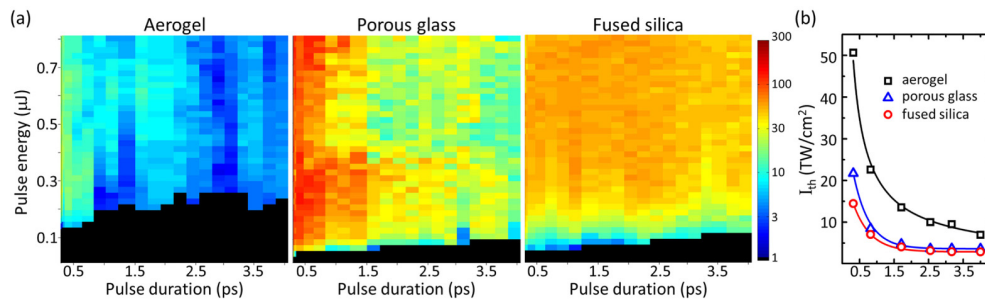


Fig. 6. (a) Laser-induced retardance in silica aerogel, porous glass (Vycor) and fused silica as a function of pulse duration and pulse energy. The retardation values were retrieved from the lines written with an interline distance of 10 μm . Polarization of the incident beam was oriented perpendicular to the writing direction. The colour bar is retardance scale in nanometres; black colour indicates the condition below the modification threshold. (b) Threshold intensity dependence on pulse duration of the laser beam focused on samples. The graphs were extracted from the retardance maps.

Threshold intensity dependence on pulse duration shows similar behaviour in all three glasses as the value decreases exponentially with the increase of pulse duration, though on average about three-fold higher pulse intensity is required to induce birefringent structures in silica aerogel [Fig. 6(b)], which could be caused by the light scattering.

4. Conclusions

In conclusion, we have demonstrated the polarization sensitive structuring of various density glasses including fused silica, porous glass, and silica aerogel. In single pulse regime, the decrease of substrate density from fused silica ($\rho_0 = 2.2 \text{ g/cm}^3$) to porous glass ($\rho_0 = 1.5 \text{ g/cm}^3$) and to silica aerogel ($\rho_0 = 0.25 \text{ g/cm}^3$) results up to tenfold increase in the laser affected region with the formation of symmetric void surrounded by the densified glass and pearl like structures, similar to water splash or supernova explosion. If the modified region is irradiated by the subsequent pulses, the transition from void to laser induced polarization sensitive structure with an orientation perpendicular to the incident polarization is observed. It was identified that the transition process takes from two to tens of pulses, and strongly depends on the initial modification caused by the first pulse. Thus, such transition is sensitive to the density of the silica substrate and could be optimized to 2-3 pulses in porous glass with pores smaller than 5 nm. As a result, the increase of retardance up to two times in porous glass compared with silica glass is demonstrated. Such ultrafast laser nanostructuring with minimized number of pulses and with significantly reduced stress could be an ideal low-cost platform for rapid prototyping, which could be explored in various fields including multi-dimensional data storage and optical component fabrication.

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